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14. ABSTRACT

This MEANS initiative research project consists of a collaborative effort between students, postdocs, and faculty at the University of Illinois and at the University of Michigan. The work involves the integration of length and time scale spanning computational methods of investigation into a suite of design tool for materials optimization. Concurrent experimental measurements serve to motivate and validate the simulation approaches. Specifically, the challenges posed by the design of autonomously healing polymer matrix composites were chosen as the test case for the development of this computational framework, which includes reactive molecular dynamics simulations, coarse-grained particle-based simulations, and cohesive-volume finite element calculations. The integration of the different methodologies is achieved through data exchange and output overlap matching. The project includes further development of specific numerical techniques, implementation of an efficient coupling mechanism, and extensive testing and validation through experiments.

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ANNUAL REPORT

For the period from 9/1/2003 to 8/31/2004

Project title:

MULTISCALE MODELING FOR THE DESIGN OF AUTONOMIC HEALING
STRUCTURAL COMPOSITE MATERIALS (MEANS)

AFOSR GRANT NO: F49620-02-1-0079

John Kieffer, PI
Department of Materials Science and Engineering
2300 Hayward Street
Ann Arbor, MI 48109-2136
Tel: (734) 763-3595; Fax: (734) 763-4788; E-Mail: kieffer@umich.edu

Abstract

This MEANS initiative research project consists of a collaborative effort between students, postdocs, and faculty at the University of Illinois and at the University of Michigan. The work involves the integration of length and time scale spanning computational methods of investigation into a suite of design tool for materials optimization. Concurrent experimental measurements serve to motivate and validate the simulation approaches. Specifically, the challenges posed by the design of autonomously healing polymer matrix composites[1] were chosen as the test case for the development of this computational framework, which includes reactive molecular dynamics simulations, coarse-grained particle-based simulations, and cohesive-volume finite element calculations. The integration of the different methodologies is achieved through data exchange and output overlap matching. The project includes further development of specific numerical techniques, implementation of an efficient coupling mechanism, and extensive testing and validation through experiments.

1. Objectives

The purpose of this project is to create a multi-scale computational framework for the design of complex materials systems by integrating molecular dynamics simulations based on a reactive force field, cohesive/volumetric finite element calculations, and a particle-based coarse-grained model to bridge the gap between atomistic and continuum modeling techniques. The particular challenge in developing this computational framework arises from the necessity to simulate the materials response to mechanical loading on a macroscopic timescale while the structural developments associated with the healing processes require resolution of mechanisms at atomic time and length scales.

While the focus for this project is on self-healing materials systems, the fundamental research pursued in this project will yield tools of analysis and experimental databases that impact materials applications beyond self-healing. The multi-scale simulations that we are developing have utility in the design of composites and multiphase materials for enhanced fatigue life and increased fracture resistance. The molecular dynamics simulations of *in situ* reaction and transport phenomena, while examining the stiffness and strength of the resulting structures, have broad applicability in the field of polymer processing and process modeling, especially in the development of structural materials.

2. Approach and Methodology

The design of self-healing materials systems requires very detailed and careful optimization of processes, including the choice of materials and repair agents based on their physical, chemical, and kinetic properties, as well as geometric and structural considerations at various levels. On the one hand, the properties of a material are very fundamentally rooted in the structure and dynamics of its atomic-scale constituents. On the other hand, the actual materials performance depends on a complex scale-spanning hierarchy of such elementary mechanisms. Incorporating atomically resolved processes in a modeling framework therefore provides for greater realism and accuracy in predicting materials behavior. At the same time one needs to keep track of how

progressions of elementary processes compound into macroscopic observables. Computationally, this requires one not only to encompass the pertinent length scales and spatial resolution, but importantly, the time scales corresponding to the reaction between molecular building blocks and to the fatigue crack propagation must be reconciled.

To create a suitable multi-scale design tool we are combining explicit-atom molecular dynamics (MD) simulations with continuum-scale cohesive/volumetric finite element (CVFE) calculations. Furthermore, to overcome the time-scale disparity between these two methods, we have developed a coarse-grained particle-based (CGP) simulation procedure that allows one to simulate atomic-scale processes in an accelerated fashion by abstracting structural detail at the building block level. CVFE is used to model fatigue crack propagation at the macro-scale. This part of the project is carried out in the group of Prof. Geubelle at the University of Illinois, while our group at the University of Michigan is working on the atomistic and intermediate-scale simulations. MD simulations are used to simulate the structural aggregation upon curing of the healing agent, determine reaction rates, and establish the relationship between mechanical properties and molecular structures at various stages of the curing process. Molecular-scale simulations furnish the loading rate dependent constitutive behavior need as input for the cohesive volume elements continuum calculations. Conversely, CVFE establishes the local conditions under which the molecular state of the material is to be evaluated.

While it is generally possible to simulate molecular structures large enough to yield local properties that are representative of the macroscopic materials behavior, a serious limitation in connecting atomistic and continuum scales arises when structural changes result from macroscopic mechanical loading that is many orders of magnitude slower than atomic motions. Particularly, the macroscopic failure process, curing rate and deformation rate in self-healing composites compete on time scales not attainable by MD simulations. Moreover, the deformation and failure may induce structural defects whose spatial extents exceed those of MD simulation boxes. Therefore, we insert an intermediate-scale lattice-based modeling approach to bridge between atomistic and continuum scales.

The development of our simulation framework is closely coupled with the experimental work of Profs. White and Sottos at the University of Illinois. This collaboration allows us to identify the design issues that need to be addressed by our numerical tools and provides us with experimental data to properly validate our modeling efforts.

3. Accomplishments

Our molecular-scale simulation approach encompasses three levels: (i) a fully atomistic level, where all atoms contained in the system are explicitly represented. At this level we determine reaction rates and structural information. (ii) a first coarse-graining level, in which larger polymeric networks are generated and the relationship between structure and mechanical properties are determined, and (iii) a second coarse-graining level, where reaction rates and deformation rates are reconciled and the overall mechanical response of the healing agent under application conditions is determined. The development of individual simulation techniques, i.e., the reactive MD simulations and the CGP model,

has been completed. The methods have been applied to study the autonomous repair behavior of self-healing polymer composites under strain.

3.1 Progress in Atomic-Scale Simulations

Polymerization and cross-linking reactions have been successfully reproduced in atomic scale simulations for systems of several hundred monomers. These simulations revealed the reaction mechanism and polymerization rates. The dicyclopentadiene (DCPD) molecule posses two reactive sites, i.e., the C=C double bonds on the buckled hexagonal ring and the pendant cyclopentenyl ring (see fig. 1). Both rings are subject to ring-opening methathesis, which is invoked by a catalyst, e.g., the transition metal complex Ru(arene)Cl$_2$(PCy$_3$).[2,3] The MD simulations using our reactive force field,[4,5] reproduce both ring opening mechanisms. Our simulations show that because the hexagonal ring is subject to significant strain, it is considerably more reactive and hence, the polymerization initially leads to linear chains. Cross-linking sets in at a slower rate, as controlled by the opening of the cyclopentenyl rings. This confirms the prevalent views concerning this mechanism as described in the literature.[2] Importantly, through simulation of the detailed bond formation processes we are able to generate a realistic model of a polymeric DCPD network, and establish its structure property relationships. In particular, using this level of simulation we can determine the reaction rate coefficient that describes the polymerization reaction. This only requires a few hundred monomers, for as long as all steric arrangements that can occur during the polymerization are represented in the simulations. This is readily achieved by studying a series of structures with different initial configurations.

Explicitly accounting for hydrogen in the simulations is costly in terms of computing times, not only because of the mere number of atoms to keep track of, but because of the small mass of hydrogen, the integration time step needs to be drastically reduced for the simulation scheme to produce accurate trajectories. Structurally, hydrogen plays a secondary role, e.g., it has negligible load bearing function, and it is therefore common practice to account for hydrogen atoms implicitly by reconfiguring CH and CH$_2$ groups

(a)   (b)

Fig. 1 Simulated DCPD molecule, (a) with all atoms represented explicitly, and (b) with hydrogen atoms treated implicitly. This reduced form of the molecule contains three types of hydrocarbon croups sp^3 CH$_2$ (red), sp^3 CH (black), and sp^2 CH (blue). Reactive sites are the double bonds between sp^2 aroups.

into unified particles, as shown in fig. 1. These new units are characterized by sizes and chemical interactions representative of the steric functionality of the groups that they replace. We have developed a model of DCPD molecules following this scheme and ascertained that the polymeric networks that form have the same geometry as those
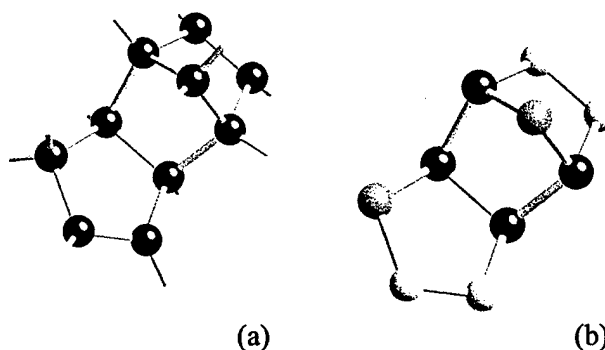
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resulting from all-atom simulations. Fig. 2 shows an example of a simulation result using this simplified model of DCPD monomers.
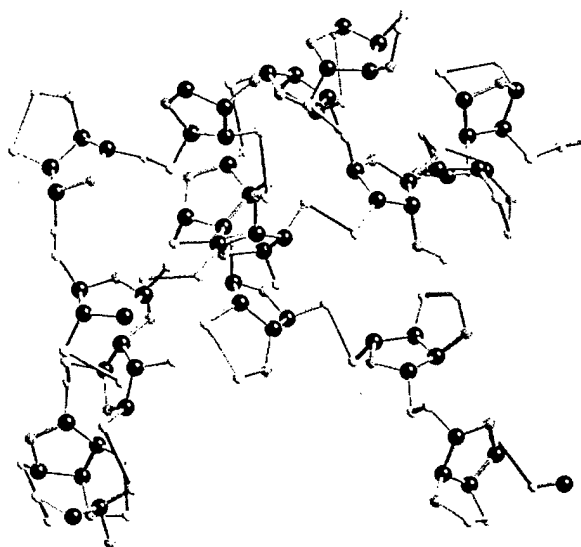

Fig. 2 Fragment of a polymerized DCPD network as generated by MD simulations based on the unified building blocj approach. Unreacted monomers are not shown for claritv.

This simplified representation of the DCPD molecule results in an increase of computational speed by nearly an order of magnitude. Accordingly, it allows for an increase in the size of simulated structures, yielding improved statistics in the description of the resulting network topologies. Based on this first coarse-graining step, we can generate polymeric networks ultimately containing several ten thousand monomers and study their structure and properties under conditions that represent all possible states the healing agent can achieve between initiation and completion of the polymerization, assuming various degrees of mechanical deformation. The important measure that results from this level of simulation is the relationship between structure and mechanical properties of the polymer network. In particular, we can determine elastic moduli and tensile strengths of networked structures at various densities. Variable density, in this case, corresponds to situations where completion of the polymerization reaction was achieved at different degrees of strain in the system.

3.2   Progress in Coarse-Grained Simulations

The simulation times that can be achieved at the aforementioned level, however, are far shorter than would be required to cover the experimental deformation rates. To realistically accommodate simultaneous deformation and polymerization as the factors contributing to the structural evolution of DCPD networks, a second level of coarse graining has been introduced, i.e., the CGP procedure. At this level, each DCPD monomer is represented by a single particle that can move about, and upon collision with other units it can undergo a polymerization reaction depending on whether the conditions for this process to occur are fulfilled. These conditions are known from atomistic simulations, and accordingly we developed statistical structural evolution rules that are implemented via a Monte Carlo numerical procedure. These rules, obviously, are designed to maintain realism in the simulated polymerization process. E.g., at least one of the particles must carry the Ru catalytic complex. Upon reaction, the Ru complex residing with the most recently polymerized unit is now transferred to the next monomer that attaches to the chain. This provides for an interesting aggregation scheme, described by the propagation of the catalyst along the growth path of the polymer. Furthermore, at

most four other units can attach to any given monomer, and we distinguish between polymerization and cross-linking reactions based on their respective rates.

Initially, we tested this concept using 2-D lattice Monte Carlo model. This proof of concept study already yielded important design information. Specifically, we found that for optimal utilization of the healing agent, it is imperative to embed the catalyst in such a way that it dissolves rapidly and be evenly distributed throughout the DCPD fluid before polymerization reaches significant degrees. Otherwise, the catalyst may become trapped and rendered ineffective. Alternatively, it may be necessary to slow the polymerization rate, e.g., by increasing the fraction of endo-modification of DCPD in the healing agent.

We have now completed the CGP method for simulation in 3-D and for particles positioned off lattice. Unreacted monomers move according to dissipative particle dynamics algorithm, which is similar to an MD algorithm, except that interactions between particles are designed to allow for larger time steps at the cost of reproducing only approximate particle trajectories. This procedure is justified when particles themselves are only approximations of molecules they represent. The chief advantage of this method is that due to the lack of conservation of dynamics, the time scale is undefined and can be synchronized with those of the reaction and deformation rates of the experiments. Synchronization is achieved by including a Monte Carlo procedure that accounts for polymerization events. I.e., at each particle collision a random selection process is invoked that results in bonding and passing of the catalyst with a probability that matches the reaction rate, as derived from all-atoms simulations (or experiments, if available). This defines the time scale, and deformation rates are adjusted accordingly.
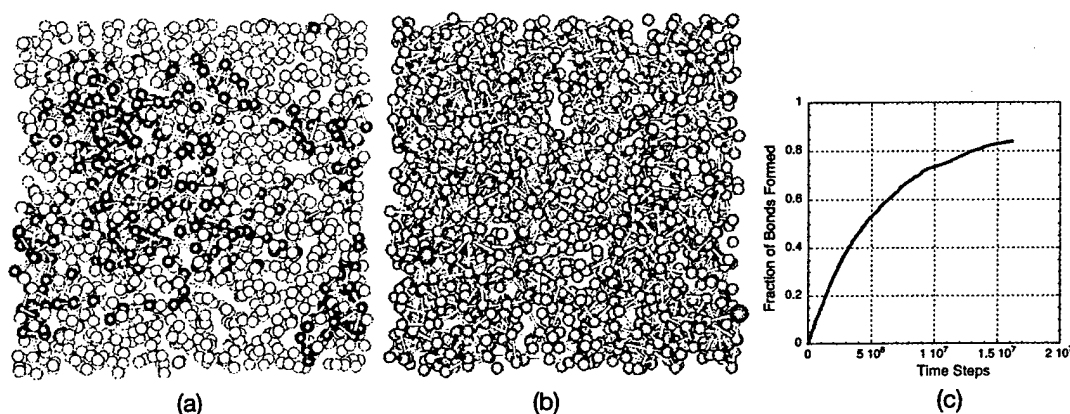

(a)   (b)   (c)

Fig. 3 (a) and (b): DCPD structures at different stages of the simulated polymerization reaction as evolved using our CGP method simulation of the DCPD polymerization process. Grey particles are unreacted monomers, blue particles are polymerized monomers, and green particles are monomers carrying the catalyst. (c) Degree of cure as a function of time.

Fig. 3 shows CGP simulation results for polymerization without deformation. The degree of polymerization changes with reaction time approximately like a first order process. The saturation level is reached between 85% and 90%, depending on the concentration of catalyst. We have furthermore simulated this process when subjecting the system to various deformation rates, which directly yields the cohesive behavior of the healing

agent, i.e., the load-deformation relationship for various cure rates, as needed as input to the CVFE calculations. Fig. 4 shows a typical result for a simulation in which the system that was cured to about 35% (i.e., just above the percolation threshold) prior to applying strain, and which is allowed to contract laterally when undergoing expansion in one direction. Note that the straining process begins at $3.1 \cdot 10^{-6}$ s. The system is already under tensile stress at this point, because it was maintained at constant volume during the initial curing phase. This initial stress can be considered as a residual stress resulting from the curing process. Fracture occurs at about 230% strain. Note the necking near the bottom of the inset showing the structures. Another interesting observation is that the reaction rate increases as soon as the strain is applied. This is because of the structural rearrangements during the deformation of the polymer network bring unreacted monomers closer to one another.
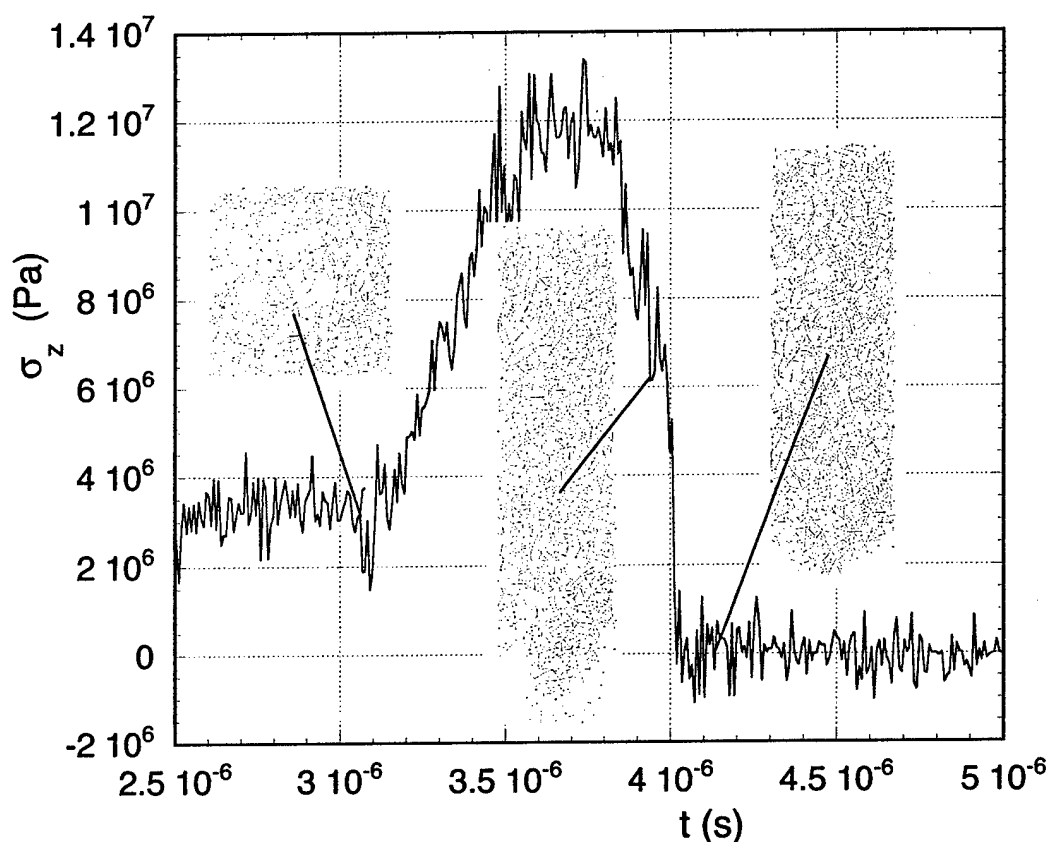

Fig. 4 Cohesive law of a DCPD system, subject to a constant strain rate of 10^8 s^{-1}. Insets show the structures at particular strain points.

4. Direction of Future Work

Currently we are systematically investigating this process to better understand the statistical mechanics of the combined cure and deformation process in self-healing

polymer matrix composites. We are exploring the effect of catalyst concentration and mobility, the ratio between polymerization and deformation rates, and the degree of cure prior to deformation.

Based on these results we will establish an effective data connection with the CVFE portion of this numerical framework. We will assess the frequency and resolution in parameter space with which the cohesive law for the self-healing polymer needs to be communicated to the CVFE calculations. We will furthermore develop an efficient procedure for integrating the calculations at different scales into a seamless suite of numerical techniques.

Finally, we plan to develop a reverse procedure to the coarse-graining at the molecular scale. As outlined above, in the CGP simulations the description of structural units and the interactions between them is simplified. To ascertain that the structural developments simulated by the CGP method are sufficiently accurate, we will develop a scheme for mapping atomically resolved structures onto the coarse-grained ones in strategic locations, and verify whether the coarse-grained structure is compatible with atomic interactions. In case discrepancies are detected, we use this information to iteratively correct the interaction and reaction rules at the coarse-grained level.

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5. Interactions/Transitions:

a. Participation

AFOSR-MEANS Bidder's Meeting, May 3, 2004, Arlington, VA

2004 AFOSR Program Review on "Mechanics of Materials and Devices." August 18-20 2004, Wintergreen Resort, VA. Presentation title: "Multiscale Modeling for the Design of Autonomic Healing Structural Composite Materials."

b. Transitions

This work constitutes a part of a multi-investigator effort to bridge length and time scales in materials simulation. Our group works on the atomic-scale and mesoscale simulation of the curing process in the healing agent of a self-healing polymer composite material under various loading conditions. The outcomes of our simulations are the constitutive law for the polymer and healing rate coefficients, which serve as input to the continuum mechanical calculations carried out by Prof. P. Geubelle and his group at the University of Illinois.

New collaborations with Dr. Ajit Roy from the Air Force Research Laboratory at Wright Patterson Air Force Base and Prof. Somnath Gosh from Ohio State University have been developed.